TITLE OF THE INVENTION:

COMPOSITIONS FOR REMOVING ETCHING RESIDUE AND USE THEREOF

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a divisional of Application Serial No. 10/191,060, filed 10 July 2002, which is incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

[0002] The present invention is concerned with selectively removing etching residues from a microstructure of an object. The present invention selectively removes residues without attacking metal and or silicon dioxide films exposed to the composition used for removing the residues. In addition, the present invention is concerned with certain cleaning compositions that are suitable for removing etching residues.

[0003] Numerous steps are involved in the fabrication of microelectronic structures. Within the manufacturing scheme of fabricating integrated circuits selective etching of semiconductor surfaces is sometimes required. Historically, a number of vastly different types of etching processes, to selectively remove material, have been successfully utilized to varying degrees. Moreover, the selective etching of different layers, within the microelectronic structure, is considered a critical and crucial step in the integrated circuit fabrication process.

[0004] Increasingly, reactive ion etching (RIE) is the process of choice for pattern transfer during via, metal line and trench formation. For instance, complex semi-conductor devices such as advanced DRAMS and microprocessors, which require multiple layers of back end of line interconnect wiring, utilize RIE to produce vias, metal lines and trench structures. Vias are used, through the interlayer dielectric, to provide contact between one level of silicon, silicide or metal wiring and the next level of wiring. Metal lines are conductive structures used as device interconnects. Trench structures are used in the formation of metal line structures. Vias, metal lines and trench structures typically expose metals and alloys such as Al, AlCu, Cu, Ti, TiN, Ta, TaN, W, TiW, silicon or a silicide such as a silicide of tungsten, titanium or cobalt. The RIE process typically

leaves a residue (of a complex mixture) that may include re-sputtered oxide material as well as possibly organic materials from photoresist and antireflective coating materials used to lithographically define the vias, metal lines and or trench structures.

[0005] It would therefore be desirable to provide a selective cleaning material and process capable of removing the residues caused by selective etching using plasmas in general and RIE specifically. Moreover, it would be desirable to provide a selective cleaning material and process, capable of removing the etching residue, that exhibits high selectivity for the residue as compared to metal, silicon, silicide and/or interlevel dielectric materials such as deposited oxides that might also be exposed to the cleaning composition.

BRIEF SUMMARY OF THE INVENTION

[0006] The present invention provides compositions capable of selectively removing etching residue from a substrate without attacking metal that might also be exposed to the composition. In addition, the present invention provides compositions that exhibit minimal silicon oxide and in general lower dielectric etch rates.

[0007] More particularly, the present invention relates to a composition suitable for removing etching residue that comprises:

A. Up to about 80% of a water miscible organic solvent;

B. About 5 to about 50% by weight of water;

C. About 1 to about 20% by weight of a dicarboxylic organic acid;

D. About 1 to about 20% by weight of a base; and

E. About 0.1 to about 10% by weight of a source of fluoride ion.

In certain embodiments, the base (D) is combined with the dicarboxylic acid (C) to form a buffering agent.

[0008] The present invention also relates to a method for removing etching residue from a substrate that comprises contacting the substrate with the above-disclosed composition.

[0009] Other objections and advantages of the present invention will become readily apparent to those skilled in this art from the following detailed description, wherein it is

shown and described only the preferred embodiments of the invention, simply by way of illustration of the best mode contemplated of carrying out the invention. As will be realized, the invention is capable of other and different embodiments, and its several details are capable of modifications in various obvious respects, without departing from the invention. Accordingly, the description and drawings are to be regarded as illustrative in nature and not as restrictive.

BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS

[0010] Figure 1 illustrates phosphorous doped un-densified TEOS etch rates of various diacid-containing formulations at the different pHs.

[0011] Figure 2 illustrates undensified undoped TEOS etch rates of various diacid-containing formulations of different pHs.

[0012] Figure 3 illustrates the PTEOS etch rates of a maleic acid buffered fluoride stripper and an aminosulfonic acid buffered fluoride stripper, both with the pH adjusted to 7.0.

[0013] Figure 4 compares the PTEOS etch rates of three products: an acetic acid buffered fluoride stripper, an aminosulfonic acid buffered fluoride stripper and example 8.

[0014] Figure 5 shows cleaning performance results on aluminum lines.

[0015] Figure 6 shows cleaning performance results on sensitive oxide vias.

DETAILED DESCRIPTION OF THE INVENTION

[0016] Compositions for removing etching residues and especially residues cased by reactive ion etching and methods comprising same are disclosed herein. Moreover, the etching residues are present in an article that also includes metal, silicon, silicate and/or interlevel dielectric material such as deposited silicon oxides and derivitized silicon oxides such as TEOS and Spin-On Glass, wherein both the residues and the metal, silicon, silicide and/or interlevel dielectric materials will come in contact with the cleaning composition. The composition selectively removes the post etch residues without significantly attacking the metal, silicon, silicon dioxide and interlevel dielectric materials. The metal is typically copper, copper alloy, titanium, titanium nitride, tantalum, tantalum nitride, tungsten, titanium/tungsten, aluminum and/or aluminum alloys. The residues

removed according to the present invention are preferably those created by reactive ion etching.

[0017] The compositions may comprise about 5 to 50% by weight, or about 20 to about 45 %, or about 25 to about 30% by weight of water. The water employed is preferably deionized water.

[0018] In addition, the compositions may contain a dicarboxylic organic acid in an amount of 1 to about 20% by weight, or about 1 to about 10% by weight, or about 2 to about 5% by weight. The dicarboxylic acids can be saturated or unsaturated, straight or branched acyclic or cyclic.

[0019] Examples of suitable saturated acyclic acids include oxalic, malonic, succinic, glutaric and adipic acids. An example of an unsaturated acid is fumaric acid or maleic acid. Examples of cyclic acids are phthalic acid and terephthalic acid. The preferred acids are succinic acid, malonic acid, maleic acid, adipic acid and phthalic acid. The more preferred acids are maleic and adipic acids and the most preferred is adipic acid.

[0020] Surprisingly, according to the present invention, the presence of dicarboxylic acids in the compositon of the invention did not result in high oxide etch rates as would have been expected, based on the acidic pH of the stripper solutions. Instead, the oxide etch rates exhibited by the compositions are at most extremely low and in some cases are almost nonexistent. It has been observed that the inhibition of oxide etching requires the diacid and/or its salt. Compositions that do not include a diacid or salt thereof fail to exhibit the oxide etching inhibition achieved by the present invention.

[0021] In addition, the compositions may contain an organic or inorganic base, which in combination with an organic diacid, forms a buffering agent; typically in an amount of about 0.5 to about 20% by weight, or about 1 to about 10% by weight, or about 2 to about 5% by weight.

[0022] The pH of these formulations can vary anywhere from 1 to about 7, or about 5.5 to 6.0 depending on the specific diacid chosen and its effective buffering range. In particular, diacids are defined by two pK_a values and a buffer is generally formed about 0.75 pH units on either side of a given pKa. For example, the pK values for malonic acid are $pK_1 = 2.8$ and $pK_2 = 5.7$. One can then expect malonic acid to act as a buffer between the pHs of 2.05 – 3.55 and again between 4.95 – 6.45. Similarly, the pK values for adipic acid are $pK_1 = 4.5$ and $pK_2 = 5.5$. Since the two pHs almost overlap, the effective

buffering range of adipic acid is between the pHs of 3.75 and 6.25. Buffering has been shown to be important because both cleaning ability and dielectric and metal etching have some dependence on pH. A pH drift can cause significant variances in cleaning and substrate etching. For example, a semiaqueous fluoride stripper at pH = 4.75 may not etch copper significantly, but at pH = 7.5 or higher may severely attack copper, causing unacceptable loss of a device critical dimension.

[0023] Examples of suitable bases include, but are not limited to: ammonium hydroxide, amines, and quaternary ammonium hydroxides. It is preferred that the base not include metal ions such as sodium and potassium since they tend to contaminate the substrate. The preferred bases are ammonium hydroxide or monoethanolamine (MEA).

[0024] Compositions may also include a fluoride ion source typically in an amount of about 0.1 to about 10% by weight, or about 0.1 to about 5% by weight, or about 0.5 to about 3% by weight. Typical compounds providing a fluoride ion source according to the present invention are hydrofluoric acid, ammonium fluoride, quaternary ammonium fluorides such as tetramethylammonium fluoride and tetrabutylammonium fluoride, fluoroborates, fluoroboric acid, tetrabutylammonium tetrafluoroborate, and aluminum hexafluoride. Also, a fluoride salt of an aliphatic primary, secondary or tertiary amine can be used. An exemplary formula is the following:

$$R_1N(R_3)R_2\,F$$

wherein R_1, R_2 and R_3 each individually represent H or an alkyl group. Typically, the total number of carbon atoms in the R_1, R_2 and R_3 groups is 12 carbon atoms or less. In certain preferred embodiments, the fluoride compound is ammonium fluoride.

[0025] The compositions may also include 0% to about 80% by weight and more typically about 1% to about 80% by weight of a water miscible organic solvent. The preferred amount of water miscible organic solvent is about 30 to about 65% by weight, or about 50 to about 60% by weight. Examples of water miscible organic solvents include, but are not limited to, dimethylacetamide, N-methyl pyrrolidinone (NMP), dimethylsulfoxide, dimethylformamide, N-methylformamide, formamide, dimethyl-2-piperidone (DMPD), tetrahydrofurfuryl alcohol, glycerol, ethylene glycol, and other amides, alcohols or sulfoxides, or multifunctional compounds, such as hydroxyamides or aminoalcohols. The preferred solvents, when employed, are dimethyl acetamide and dimethyl-2-piperidone and N-methylpyrrolidinone.

[0026] Also, if desired, the composition can optionally include a corrosion inhibitor. When present, the corrosion inhibitor is employed typically in amounts up to about 10% by weight, or about 0.5 to about 5% by weight, or about 1 to about 2% by weight. Examples of corrosion inhibitors include, but are not limited to catechol, gallic acid, benzotriazole, resorcinol, other phenols, acids or triazoles.

[0027] In certain embodiments, it is preferred that the compositions of the present invention, when used on substrates containing copper do not contain benzotriazole which has a tendency to bind to copper surfaces. Benzotriazole is present in various prior art compositions.

[0028] Some examples of substrate compositions of the present invention are illustrated below in Table 1 and preferred compositions are illustrated in Table 2.

Table 1

Component	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12
Dimethyl-acetamide	60	60	60	60	60	60	60	60	60	60	60	60
Water	29.8	31.3	29.3	30.8	33.55	32.55	31.75	30.85	33.5	34.75	31.59	30.5
Succinic Acid	4	4					4	4	4			
Malonic Acid			3.5	3.5								
Adipic Acid					3					3		
Phthalic Acid						4						
Maleic Acid											4	4
28% NH4OH	3.7	3.7	4.7	4.7	2.2	2.6	3	3.9	1.25	1	3.16	4.25
40% NH4F	2.5	1	2.5	1	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25
pH (5 % sol'n)	5.44	5.42	5.72	5.41	5.67	5.7	5.36	6.17	4.39	4.77	6.15	7
PTEOS etch rate							17.94	4.25	64	38.55	1.35	0.29

Table 2: Preferred Formulations

Component	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12
dimethylacetamide	60	60	60	60	60	60
DI water	29.8	31.05	27.3	34.75	33.75	32.5
maleic acid	4	4	4	4		
adipic acid					3	3
monoethanolamine					2	2
28% ammonium hydroxide	3.7	3.7	3.7			
40% ammonium fluoride	2.5	1.25	5	1.25	1.25	2.5
pH (5% solution)	6.48	6.59	6.55	2.37	5.6	5.5

[0029] Table 3 below shows selected acid pKa values and expected effective buffering ranges.

Table 3: Acid pKa Values and Effective Buffering Range

Diacid	Mol. Wt.	pK1; pK2	Buffering Range
Oxalic	90.04	1.27; 4.27	0.52 – 2.02; 3.52 – 5.02
Malonic	104.06	2.8; 5.7	2.05 – 3.55; 4.95 – 6.45
Succinic	118.09	4.2; 5.63	3.45 – 6.38
Glutaric	132.12	3.8; 6.08	3.05 – 4.55; 5.33 – 6.83
Adipic	146.14	4.4; 5.4	3.65 – 6.15
Maleic	116.07	1.9; 6.3	1.15 – 2.65; 5.55 – 7.05
Fumaric	116.07		
Phtalic	166.13		
Acetic	60.05	4.75	4.0 – 5.5
Acrylic	72.06		
HEPES	238.31	7.6	6.85 – 8.35

[0030] The foregoing description of the invention illustrates and describes the present invention. Additionally, the disclosure shows and describes only the preferred embodiments of the invention but, as mentioned above, it is to be understood that the invention is capable of use in various other combinations, modifications, and environments and is capable of changes or modifications within the scope of the inventive concept as expressed herein, commensurate with the above teachings and/or the skill or knowledge of the relevant art. The embodiments described hereinabove are further intended to explain best modes known of practicing the invention and to enable others skilled in the art to utilize the invention in such, or other, embodiments and with the various modifications required by the particular applications or uses of the invention. Accordingly, the description is not intended to limit the invention to the form disclosed herein. Also, it is intended that the appended claims be construed to include alternative embodiments.